Preparation and Characterization of Nanoscale Silver Colloids by Two Novel Synthetic Routes

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We report the results of treating a dense, chemically produced silver colloidal suspension with high-power laser pulses and with exposure to supercritical water (SCW) conditions. The initial colloid has a mean particle diameter measured by transmission electron microscopy to be 28.4 nm and exhibits a broad absorption band in the visible region with a small maximum near 420 nm. Both treatments result in smaller particles. The laser treatment fragments the original colloidal particles and produces an average particle diameter of 5.4 nm. The SCW treatment appears to dissociate aggregates in the original colloid, resulting in particles with a mean diameter of 9.9 nm. Plasmon resonances for the two colloids produced by these treatments appear at 400 nm and 390 nm for laser- and SCW-treated colloids, respectively. The plasmon resonance of the laser-treated colloid is typical of small silver colloids produced by most methods, whereas the 390-nm resonance of the SCW-treated colloid implies a strongly negative colloidal surface charge. © 2001 Academic Press

Key Words: colloid; silver; SERS; ablation; supercritical; nanoscale.

INTRODUCTION

Metallic silver colloids were first prepared more than a century ago (1). Since the discovery of surface-enhanced Raman spectroscopy (SERS) in the mid-1970s (2), Ag colloids have been regularly used as substrates for SERS (3). Several studies have revealed that surface enhancement of the Raman modes for various adsorbates is widely influenced by the size and shape of colloidal particles and their state of aggregation (4–10).

The most frequent preparation of Ag colloids is by chemical reduction of silver salts by sodium borohydride (11) or sodium citrate (12). Although this preparation is simple, great care must be exercised to make a stable and reproducible colloid. The purity of the water and reagents, as well as the cleanliness of the glassware, are critical parameters (13, 14). Solution temperature, concentrations of the metal salt and reducing agent, and reaction time all influence particle size (14, 15). The sedimentation of large Ag particles in these colloids can cause an undesirable temporal dependence of the optical characteristics of the colloids (16) and complicates particle size determinations by light scattering methods. More homogeneous suspensions can be produced by particle fractionating via centrifugation, prolonged sedimentation, and other means, but these fractionating techniques have drawbacks of their own (4, 6, 14).

In our laboratory, we have recently made an effort to study the properties of Ag colloids as potential substrates for catalysis and photocatalysis. During these measurements, we observed changes in the optical characteristics of chemically produced colloidal suspensions indicative of changes in the particle size distributions. These changes were produced by two different means.

In the first approach, excitation of a colloidal suspension of chemically produced colloids with light from a high-powered Nd:YAG pulsed laser fragments larger colloid particles. The effect is remarkable and obvious to the unaided eye, as a milky gray-yellow colloidal suspension converts into a dense, clear yellow suspension. Similar studies have recently been conducted by Kamat et al. (17).

In the second approach to modifying Ag colloids, supercritical water (SCW) is used to fragment large colloidal particles. Dense, milky gray-yellow chemically reduced colloidal suspensions introduced to a SCW reactor for short times emerged from the reactor as transparent yellow suspensions. Atomic absorption measurements on washings from the reactor indicated that negligible precipitation of the metal had occurred in the reactor.

Details of these two preparations and characteristics of the colloids produced by these methods are reported below.

MATERIALS AND METHODS

Preparation of the Sols

Analytical grade chemicals obtained from Sigma Aldrich (Milwaukee, WI) and redistilled deionized water (specific resistance 18 MΩ/cm) were used for all sample preparations. The colloids were prepared according to Taylor et al. (18) by introducing sodium citrate (3 mL, $4.42 \times 10^{-1}$ M) drop-wise over a 1-h period to a boiling solution of silver nitrate (500 mL, $3.83 \times 10^{-3}$ M) with vigorous stirring. The solution was then boiled for a subsequent hour, and this solution was returned to 500 mL after cooling.
Scanning transmission electron microscopy (TEM) grids were prepared at each interval for each sample with a diode-array UV–vis spectrophotometer. This experiment was repeated three times with three separate reactors. For calibration, a 500 mg/L Ag⁺ solution was prepared by dissolving 78.7 g AgNO₃ in 50 mL of e-pure water. This solution was then diluted to 1 L with 1% v/v HNO₃ and stored in an amber bottle wrapped with aluminum foil. Silver standards were prepared by diluting this solution with 5% v/v HNO₃ to keep the silver in solution. Supercritical water can be an effective medium for oxidation. To test whether any silver metal had been oxidized back to Ag⁺ in the reactor, a 3 × 10⁻² M solution of NaBH₄ was slowly added to the silver colloid removed from the reactor to test for further reduction. None was observed.

RESULTS AND DISCUSSION

Laser-Induced Fragmentation

The colloid as initially prepared by chemical reduction had broad absorption bands in the visible spectral region with a weak maximum at 420 nm and another at 550 nm. After 2 min of treatment with the laser, the peak at 420 nm became slightly more intense. With each pulse of the laser, the colloid directly in the beam path turned deep amber in color; the change in the colloid was immediate and visible to the naked eye. With stirring this ablated zone would mix into the surrounding suspension, bringing fresh colloid into the laser beam. Sequential measurements at 2-min intervals showed a monotonic increase in the high-energy absorbance intensity as well as a shift in this high-energy peak toward 400 nm (Fig. 2). As this peak grew in intensity, the peak at 500 nm diminished. Previous work in other laboratories suggests that this 400-nm peak is characteristic of elementary spherical Ag particles (2, 4). at the open-circuit potential of +0.15 V vs. Ag/AgCl that is produced by irreversible oxygen reduction at metal surfaces (2). This is consistent with our observation. TEM micrographs of the laser-fragmented colloid were analyzed to produce the size distribution information presented in Table 1. Figure 3a is an image of the original, chemically prepared particles. The mean diameter, $D_m$, was 28.43 nm, and the histogram in Fig. 3a reveals a wide particle size distribution.
FIG. 2. Absorption spectra in the UV–vis spectral window of colloids treated with pulsed laser excitation and SCW. Each solid-line spectrum is acquired at 2-min intervals during laser treatment of an initial chemically prepared colloid. The curve labeled “0 minutes” is the spectrum of the chemically prepared colloid before laser treatment. The dashed line is the spectrum of the colloid removed from a SCW reactor starting with the same initial chemically prepared colloid. It has been offset for clarity.

range for these particles. The weight average mean diameter as defined by

\[
D_{\bar{w}} = \sqrt{\frac{\sum_i (n_i D_i^3)}{\sum_i (n_i D_i^1)}}
\]

was calculated to be 37.64 nm. After 16 min of irradiation, the particles in our study decreased to an average diameter of 5.38 nm and fell into a size distribution ranging between 2 and 12 nm in diameter. Figure 3b shows a TEM image and size distribution histogram of the laser-treated colloid. Little change in particle size or shape was noted with additional laser exposure.

<table>
<thead>
<tr>
<th>Colloid description</th>
<th>(D_n) (\text{nm})</th>
<th>(D_w) (\text{nm})</th>
<th>(\lambda_{\text{max}}) (\text{nm})</th>
<th>(\Delta W_{1/2}) (\text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically prepared</td>
<td>28.43</td>
<td>37.64</td>
<td>1.32</td>
<td>420</td>
</tr>
<tr>
<td>After 6-min laser treatment</td>
<td>21.13</td>
<td>28.88</td>
<td>1.38</td>
<td>405</td>
</tr>
<tr>
<td>After 10-min laser treatment</td>
<td>5.83</td>
<td>8.62</td>
<td>1.48</td>
<td>400</td>
</tr>
<tr>
<td>After 16-min laser treatment</td>
<td>5.38</td>
<td>8.69</td>
<td>1.62</td>
<td>400</td>
</tr>
<tr>
<td>After SCW treatment</td>
<td>9.87</td>
<td>16.66</td>
<td>1.64</td>
<td>390</td>
</tr>
</tbody>
</table>

\(\text{a} \quad D_n = \text{number average mean diameter.}\)  
\(\text{b} \quad D_w = \text{weight average mean diameter.}\)  
\(\text{c} \quad U = \text{uniformity.}\)  
\(\text{d} \quad \Delta W_{1/2} = \text{half-width at half-maximum.}\)

The absorption spectrum also stops changing after about 18 min of irradiation (Fig. 2).

In addition to the quantifiable changes observed in the absorption spectra and particle size distributions, we also noted that the laser-fragmented colloids had a low affinity for aggregation. Particles made in the initial chemical reduction process have a strong affinity for one another, and aggregates are present or form during the process of drying on the copper TEM grid as seen in Figs. 3a and 3b. As these particles are exposed to longer laser radiation treatments, the number of aggregates diminishes and smaller isolated particles are observed on the TEM grids. These smaller particles with diminished aggregation exhibited long shelf lives; refrigerated colloids made by laser-induced fragmentation were stable and unchanging for several months. The original, chemically prepared colloid...
undergoes pronounced sedimentation after several days under similar conditions, with maximum storage of only 2–3 weeks. To address the question of whether we are observing a simple breakdown in particle size or a photo-induced charge accumulation, NaBH₄ was added to the original colloid with an absorbance maximum at 420 nm. This agent transfers electrons resulting in a negatively charged colloid and should result in breakup of large aggregates. The effect on the absorbance band was a slight blue shift to 400 nm and a dampening effect on intensity.

**Exposure to Supercritical Conditions**

The chemically prepared colloid exposed to supercritical conditions for 20 min appeared a medium amber color when removed from the reactor, exhibiting a blue-shifted plasmon resonance centered at 390 nm. TEM images reveal particles intermediate in size between the original untreated colloid and the laser-fragmented colloidal material, with a mean particle diameter of 9.87 nm and a weight-average mean diameter of 16.66 (Table 1). The size distribution for this colloid is thus broader than for either the original or the laser-treated colloid. Figure 4 is a representative TEM image with the corresponding histogram for 200 particles from the SCW sample.

The peak position of the plasmon resonance absorbance for the SCW-treated colloid suggests a negatively charged colloid. Reference (2) reports that the absorption maximum of silver colloidal particles can be shifted reversibly from 404 nm to 392 nm by varying their potential electrochemically from positive to negative, respectively. The spectroscopic limits in Ref. (2) correspond to the positive potential required for oxidation of the particles to Ag⁺ and the negative potential required for hydrogen evolution. The particles resulting from SCW treatment are distinct from the colloids in Ref. (2) in two ways. First, the absorption maximum is at higher energy than any charged colloid observed in that reference, implying a more negative potential. Second, the negatively charged colloids produced in Ref. 2 discharged back to an open-circuit potential of +0.15 V vs Ag/AgCl rapidly. The colloids produced by SCW treatment are stable for extended periods.

Because others have produced very small colloids in which the plasmon resonance appears to stop moving to higher energy below a particular size threshold (10), the shift in the plasmon resonance cannot be solely attributed to reduction in size. In addition, others have produced silver colloids by alternative methods that exhibit the same spectroscopic behavior as the citrate-reduced colloid (10, 16); therefore, this behavior is not explained by loss of citrate. We feel these SCW produced particles are unique by
their ability to maintain the higher negative potential as stable colloids.

We have attempted to address the question of how SCW produces smaller silver particles from the starting colloid. At least two possibilities exist that seem reasonable. The first is a simple, thermodynamically driven breakup of aggregates in the original colloid. The second is dissolution of silver in SCW, followed by reprecipitation.

To test this second hypothesis, 2.04 mg of sterling silver were placed in the reactor with 4 mL of water. This amount of silver is equivalent to the amount of silver in 4 mL of the chemically prepared colloidal suspension. The reactor was heated to supercritical conditions, held at temperature for 50 min to give time for the silver to dissolve and then returned to room temperature. The silver metal was quantitatively recovered from the reactor, indicating that dissolution and reprecipitation as a colloid was not occurring. In a test to ensure that no silver precipitated onto the reactor walls during the SCW process, the reactor was washed with a 10% v/v nitric acid solution for a 24-h period, and the washings were analyzed via atomic absorption spectroscopy. The maximum silver recovered from the three reactors was 83 μg, approximately 4% of the total silver introduced to the reactor. From these experiments we conclude that most of the Ag metal introduced to the reactor remains either suspended or dissolved in the liquid phase on removal. The absence of any new precipitate on addition of more reducing agent indicates that silver is not converted to Ag⁺. The strongly blue-shifted absorbance of the SCW colloid suggests a strong overall negative charge on the colloidal particles. Since dissolution and reprecipitation appear negligible, we conclude that dispersal of colloidal aggregates in the original colloid is responsible for the decreased average particle size in the SCW-treated colloid. The strong charge created on the colloidal particles during SCW treatment may account for breakup of weakly bound aggregates.

**Polydispersity**

One measure that has been used to characterize the size distribution in a polydisperse system is the uniformity, $U$, defined in Eq. [2]:

$$U = \frac{D_\phi}{D_\delta}. \quad [2]$$

Size distribution is only considered monodisperse when $U \leq 1.01 (10)$. Although both laser and SCW treatments narrow the full-width at half-maximum of the distribution in absolute terms, both also reduce the average particle size and thus increase the uniformity value.

The weight average mean diameter and thus the uniformity are both highly influenced by the presence of large particles, and all the colloidal suspensions reported here are polydisperse. Because the laser fragmentation process is very localized, uniformity calculations on the fragmented colloids reveal that the colloidal suspensions become more polydisperse as the average particle diameter decreases. This is likely because some of the large colloidal particles in the original suspension are never fragmented (or only partially fragmented) because they never (or only rarely) passed through the laser path during processing.

The uniformity of the SCW-treated colloid is likely a reflection of the true uniformity of the original chemical reduction procedure, because it seems likely that the colloid removed from the SCW reactor is only the result of dissociation of the colloidal aggregates.

**CONCLUSIONS**

Two new treatments for silver colloids that result in smaller size distributions have been described in this report. Our initial efforts to extend these methods to other metals (notably platinum and palladium) have been met with much less success. Rather than producing stable colloids, laser and SCW treatments of these other metals tend to cause the particles that are formed to aggregate and precipitate from suspension in our experiments.

The nature of the colloidal surfaces following these treatments is currently unknown. The strong hypsochromic shift observed on SCW treatment suggests that the surfaces of the silver colloidal particles are strongly negatively charged and should discharge via hydrogen production in aqueous suspension. The fact that they do not suggests that either the solution is a strongly reducing environment after removal from the reactor or that the surface is passivated in some way.

We note in closing that these colloids have not yet shown activity as substrates for SERS. Both colloidal suspensions respond quickly to the addition of salts or pyridine by turning blue and aggregating, but thus far we have been unable to record any surface-enhanced Raman spectra from these blue suspensions. This lack of SERS activity is possibly due to the same unique surface chemistry that allows these colloids to retain their negative charge while maintaining a long, stable shelf-life.

**ACKNOWLEDGMENTS**

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